



Short communication

Determination of methylamines and trimethylamine-*N*-oxide in particulate matter by non-suppressed ion chromatographyMark E. Erupe^a, Allegra Liberman-Martin^b, Philip J. Silva^{a,c}, Quentin G.J. Malloy^d, Naomi Yonis^b, David R. Cocker III^d, Kathleen L. Purvis-Roberts^{b,*}^a Department of Chemistry and Biochemistry, 0300 Old Main Hill, Utah State University, Logan, UT 84322-0300, USA^b Joint Science Department of Claremont McKenna, Pitzer, and Scripps Colleges, W.M. Keck Science Center, 925 N. Mills Ave., Claremont, CA 91711, USA^c USDA-ARS, 230 Bennett Lane, Bowling Green, KY 42104, USA^d Department of Chemical and Environmental Engineering and College of Engineering, Center for Environmental Research and Technology (CE-CERT), University of California, Riverside, CA 92521, USA

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ABSTRACT

An ion chromatography method with non-suppressed conductivity detection was developed for the simultaneous determination of methylamines (methylamine, dimethylamine, trimethylamine) and trimethylamine-*N*-oxide in particulate matter air samples. The analytes were well separated by means of cation-exchange chromatography using a 3 mM nitric acid/3.5% acetonitrile (v/v) eluent solution and a Metrosep C 2 250 (250 mm × 4 mm i.d.) separation column. The effects of the different chromatographic parameters on the separation were also investigated. Detection limits of methylamine, dimethylamine, trimethylamine, and trimethylamine-*N*-oxide were 43, 46, 76 and 72 μg/L, respectively. The relative standard deviations of the retention times were between 0.42% and 1.14% while the recoveries were between 78.8% and 88.3%. The method is suitable for determining if methylamines and trimethylamine-*N*-oxide are a significant component of organic nitrogen aerosol in areas with high concentration of these species.

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1. Introduction

Organic nitrogen is ubiquitous in the environment, and yet a poorly characterized component of atmospheric aerosol [1–3]. With growing concerns of aerosol effects on health, climate and modification of the nitrogen cycle, it is crucial to identify sources as well as understand the composition of atmospheric aerosol, including the organic nitrogen component [4–6]. Previous studies of organic nitrogen in the atmosphere have concentrated on dissolved organic nitrogen [7]. Most of these were bulk studies where the total water soluble organic nitrogen was determined, and compound-specific studies of organic nitrogen aerosol remain rare [8–10]. Given the diversity of the organic nitrogen compounds, it has been difficult to define source-and-sink budgets and describe their atmospheric behavior. This knowledge demands both the quantitative determination of bulk organic nitrogen aerosol and the characterization of individual compounds.

Agricultural practices are known to input large amounts of nitrogenous species into the atmosphere [11]. Some of these compounds react using a number of pathways to form gas phase species

as well as aerosol. Most studies have focused on the inorganic nitrogen chemistry, especially the contribution of ammonia in aerosol formation, but the organic nitrogen fraction of the aerosol is important as well. Recent work has shown that some organic species such as aliphatic amines may be present in concentrations as high if not greater than that of ammonia [12,13]. These species could therefore undergo atmospheric reactions to form secondary organic nitrogen containing aerosol.

Several researchers have detected amines in aerosols during ambient air sampling [14–16]. Some of these studies have indicated that amine cations are present in aerosols as salts formed in secondary reactions in the atmosphere [14,15]. One ambient study using aerosol mass spectrometry (AMS) showed significant particle mass loadings of up to 6 μg m⁻³ [16]. Smog chamber reaction studies focusing on amines have also been performed to characterize the types of amines present in aerosol products due to atmospheric oxidation [8,16–18]. Amine-*N*-oxides were first hypothesized as a potential reaction product of tertiary amines in a smog chamber study using aerosol time-of-flight mass spectrometry (ATOFMS) [8]. Other reports have shown that the reaction products of amines can be a complex mixture of salt formation products and/or secondary organic oxidation species [16]. Recent studies using the AMS have indicated that little of the aerosol product can be accounted for by the formation of salts [17,18]. Clearly, a separation method that

* Corresponding author. Tel.: +1 909 607 9782; fax: +1 909 621 8588.
E-mail address: kpurvis@jcd.claremont.edu (K.L. Purvis-Roberts).

can sort through some of these proposed reaction products would be helpful to corroborate observations using mass spectrometry.

Trimethylamine-*N*-oxide (TMAO) is a natural osmolyte found in some marine creatures such as fish [19]. When fish rots, TMAO is enzymatically converted to TMA that gives the characteristic 'fishy' smell. It has been suggested that TMAO may also form in the atmosphere through oxidation of trimethylamine by ozone and other oxidants [8,16]. This reaction would be important in areas where the mixing ratio of trimethylamine is thought to be high due to the presence of agricultural emissions such as the central valley of California and Cache Valley in northern Utah. There have been no attempts to measure TMAO in atmospheric aerosol.

An efficient and simple method is necessary for the quantitative determination of TMAO in air samples. Here we report a method that can be used to detect and quantify TMAO and methylamines in air samples using non-suppressed ion chromatography. The composition of the mobile phase was optimized and efficient separations between the analytes were achieved. A variety of analytical techniques have been developed to measure biogenic amines in food samples. For example, ion chromatography with suppressed conductivity detection with either integrated pulsed amperometric or conductimetric detection has been utilized to measure amines such as putrescine, cadaverine, histamine, and similar compounds in alcoholic beverages, fresh and processed meats, chocolate, fish, vegetables, and fermented foods [20–25]. A gradient elution method coupled with suppressed ion chromatography was used to separate alkylamines, such as butylamine and diethylamine, from alkali and alkali earth metals [26]. A study of dimethylamine, trimethylamine and TMAO separation using non-suppressed conductivity applied to aquatic products was recently published [27]. To our knowledge, this study is the first application of IC non-suppressed conductivity detection to analyze TMAO in addition to methylamine, dimethylamine, and trimethylamine in aerosol samples.

The main goal of this study is to develop a method to determine whether TMAO is a quantitatively significant component of organic nitrogen aerosol in the atmosphere. This is done using aerosol collected from smog chamber reactions of trimethylamine with ozone and/or nitrogen oxide. The method is tested using a solution of laboratory-generated aerosol containing a mixture of the analytes.

2. Experimental

2.1. Materials and chemicals

All the reagents used in this study were of analytical reagent grade. Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA) to produce 18.2 M Ω water. Methylamine hydrochloride (98%, Sigma), dimethylamine hydrochloride (99%, Aldrich), trimethylamine hydrochloride (98%, Aldrich), trimethylamine-*N*-oxide dihydrate (98%, Acros), nitric acid (90%, Sigma), and acetonitrile (99.9%, Fisher) were all used as purchased.

2.2. Chromatography

Ion chromatography was performed using a Metrohm 761 Compact IC instrument with non-suppressed detection (Metrohm-Peak, Houston, TX). The IC was equipped with a dual-piston pump, a degas assembly, and digital conductivity detection. Analysis was accomplished with a Metrohm-Peak Metrosep C 2 250 column (250 mm \times 4 mm i.d.) with metrosep RP guard column (with steel mesh filters), which was chosen because of its advantage in the analysis of amines as well as common inorganic cations with non-suppressed conductivity detection. The optimized eluent solution contained 3 mM nitric acid/3.5% (v/v) acetonitrile solution at a flow rate of 1.0 mL/min. Data processing was performed with IC Net

2.3 software. The samples were injected manually from a 500 μ L sample loop and analyzed in 15-min increments. Separation was carried out under isocratic conditions and at a room temperature of approximately 20 $^{\circ}$ C.

2.3. Preparation of standard and sample solutions

A mixed standard solution of methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and trimethylamine-*N*-oxide (TMAO) was prepared by dissolving reagent grade methylamine hydrochloride, dimethylamine hydrochloride, trimethylamine hydrochloride, and trimethylamine-*N*-oxide dihydrate in high-purity 18.2 M Ω Millipore water. The stock solution contained 6.5 mg/L MA, 13 mg/L DMA, 15.5 mg/L TMA, and 20.5 mg/L TMAO. The stock solution was stored in an HDPE container at 5 $^{\circ}$ C. Standards for calibration were prepared by diluting the stock solution with Millipore water.

Filter samples from the smog chamber were extracted into 10.00 mL of Millipore water after sonicating for 30 min. The samples were injected into the ion chromatograph without further dilution. Sample solutions were stored in glass containers that had been rinsed multiple times with Millipore water and refrigerated overnight at 5 $^{\circ}$ C.

3. Results and discussion

3.1. Standard separation

A straight forward, rapid method has been developed for determination of organic nitrogen in aerosols using non-suppressed ion chromatography. A chromatogram of a standard solution of methylamines and methylamine-*N*-oxide is shown in Fig. 1. The analytes are well separated in less than 15 min. Separation selectivity of the TMA and TMAO was reversed in comparison to the work done by Li et al. due to the use of a different IC column [27].

Under optimized experimental conditions, all four analytes showed good linearities between the concentrations and peak height responses. The limits of detection (LOD) were based on the calibration curves using three times the average baseline noise ($S/N = 3$). Results from the standard separation are listed in Table 1.

3.2. Lab sample determination

In order to illustrate an application of the developed method, two filter samples were analyzed that were obtained from simulated atmospheric chemical reactions in a controlled smog chamber. Trimethylamine was introduced into a smog chamber by

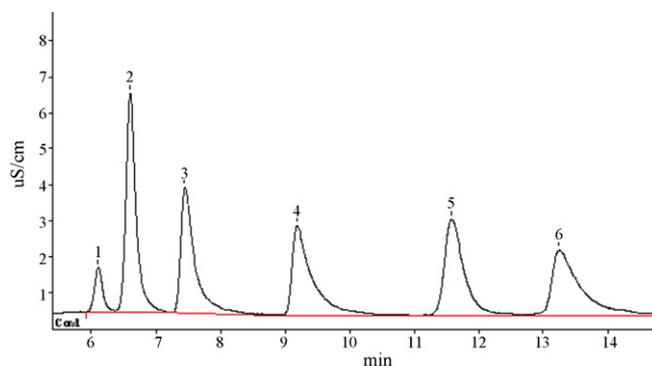


Fig. 1. Separation of methylamines and methylamine-*N*-oxides from standard solutions. Analytes: 1-sodium, 2-ammonium, 3-methylamine (195 μ g/L), 4-dimethylamine (390 μ g/L), 5-trimethylamine-*N*-oxide (465 μ g/L), and 6-trimethylamine (615 μ g/L).

Table 1
Precision and accuracy data for methylamines and trimethylamine-*N*-oxide.

Analyte	Range ($\mu\text{g/L}$)	Linearity	LOD ($S/N=3$) ($\mu\text{g/L}$)	Retention time (min)	SD (min)	RSD (%)	Peak height ($\mu\text{S/cm}$)	Peak height SD ($\mu\text{S/cm}$)	RSD (%)
Methylamine	130–390	0.9975	43	7.45	0.03	0.42	4.85	0.02	0.43
Dimethylamine	260–780	0.9999	46	9.19	0.07	0.81	3.54	0.05	1.35
Trimethylamine- <i>N</i> -oxide	410–1230	0.9999	72	12.00	0.08	0.73	3.87	0.05	1.32
Trimethylamine	310–930	0.9988	76	13.27	0.15	1.14	2.41	0.03	1.07

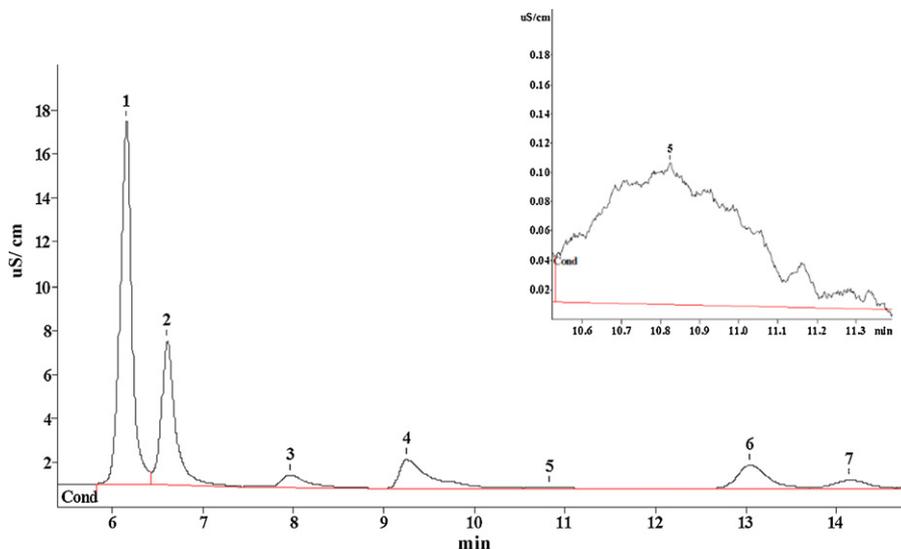


Fig. 2. Chromatogram of smog chamber filter analysis from reaction of trimethylamine with ozone. Analytes: 1-sodium, 2-ammonium, 3-potassium, 4-dimethylamine ($1.72 \mu\text{g/m}^3$), 5-trimethylamine-*N*-oxide ($0.25 \mu\text{g/m}^3$), 6-magnesium, and 7-trimethylamine ($0.57 \mu\text{g/m}^3$). The inset is a magnification of the trimethylamine-*N*-oxide peak (5) from the chromatogram.

passing a gentle stream of pure nitrogen gas over a known amount of liquid trimethylamine which is swept into the smog chamber. Addition of oxidants to the chamber (either ozone or ozone and nitrogen oxide) then proceeded to commence aerosol formation. The resulting aerosol was collected on Teflon filters by pumping the aerosol produced in the smog chamber through the filters. These filters were kept in a freezer at approximately -20°C for two days before they were extracted with Millipore water for analysis with the IC non-suppressed method described above. For a detailed description of the smog chamber set-up, refer to Carter et al. [28].

Figs. 2 and 3 present the spectra of smog chamber generated aerosol samples, one using solely ozone as the oxidant (**Fig. 2**) while the other used a combination of ozone and nitrogen oxide (**Fig. 3**). It is well known that dark reactions between ozone and nitrogen oxide lead to production of NO_3 . The aerosol generated in these experiments has been previously shown to be chemically identical to that generated by direct oxidation of NO_3 formed from the thermal decomposition of N_2O_5 [16]. All of the analytes present in the smog chamber samples were detected and quantified, although no methylamine was generated in the ozone oxidation sample and no trimethylamine was produced in the ozone and nitro-

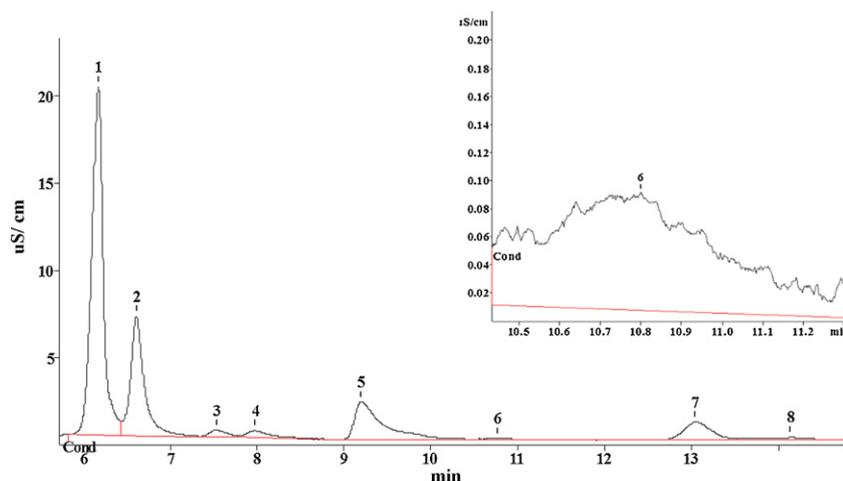


Fig. 3. Chromatogram of smog chamber filter analysis from reaction of trimethylamine with ozone and nitrogen oxide. Analytes: 1-sodium, 2-ammonium, 3-methylamine ($0.10 \mu\text{g/m}^3$), 4-potassium, 5-dimethylamine ($2.51 \mu\text{g/m}^3$), 6-trimethylamine-*N*-oxide ($0.22 \mu\text{g/m}^3$), 7-magnesium, and 8-trimethylamine ($0.21 \mu\text{g/m}^3$). The inset is a magnification of the trimethylamine-*N*-oxide peak (6) from the chromatogram.

Table 2Precision and accuracy data in smog chamber generated methylamine aerosol samples ($n=4$) and laboratory percent recovery studies ($n=4$).

	Trimethylamine + O ₃			Trimethylamine + O ₃ + NO			Laboratory-generated aerosol		
	Amount found (μg/m ³)	SD (μg/m ³)	RSD (%)	Amount found (μg/m ³)	SD (μg/m ³)	RSD (%)	Measured (mg/L)	Actual (mg/L)	Recovery (%)
Methylamine	<DL ^a	–	–	0.10	0.001	1.35	16.10	20	80.5
Dimethylamine	1.72	0.03	1.81	2.51	0.03	1.35	16.92	20	84.6
Trimethylamine- <i>N</i> -oxide	<DL	–	–	<DL	–	–	52.98	60	88.3
Trimethylamine	0.57	0.05	8.36	<DL	–	–	47.28	60	78.8

^a <DL, less than the detection limit.

gen oxide sample (Table 2). In addition, concentrations of the trimethylamine-*N*-oxide were below the detection limits in both samples. The dimethylamine peaks in both samples have a slightly larger tail than the standard spectra. This could be due to a small peak amine oxidation product formed in the smog chamber that co-elutes with the DMA. The smog chamber experiments indicate that trimethylamine-*N*-oxide does not make up a significant portion of product as it would be readily detected from the non-suppressed IC method, under these oxidation conditions. Sodium, potassium, and magnesium contamination from the glassware used for extraction is evidenced in both samples and was observed in the blank filter analyses as well. In a location such as Logan, Utah with concentrations of alkylamines and trimethylamine-*N*-oxide on the order of several μg/m³ in the air, the LOD using non-suppressed IC for these compounds (between 0.022 and 0.040 μg/m³ in the air) is low enough for detection. This calculation is based on the PM2.5 Federal Reference Method of a 24 h sampling time at 16.67 liters per minute, and takes into account the percent recovery of the amines (Table 2).

Table 2 also provides the summary of the results from lab generated aerosol samples for percent recovery studies. The samples were obtained by atomizing a solution containing the methylamines and TMAO onto pre-weighed filters then extracting the filters with Millipore water before injection into the ion chromatograph. Sample recoveries, calculated by dividing recovered amine by the actual amount of amine in the original sample, of between 78.8% and 88.3% were achieved.

4. Conclusion

A method for the simultaneous determination of methylamines and TMAO was developed using ion-exchange chromatography with non-suppressed detection. The method described here is simple and has low detection limits suitable for analysis of aerosols generated in smog chamber experiments and in ambient air where the concentration of these species is expected to be high. The smog chamber samples indicate that only minor amounts of particulate amines (1.5%) can be accounted for by the cation salts and amine-*N*-oxides. If these observations hold true for ambient sampling, it would indicate that particulate amines may be dominated by chemistry other than acid–base interactions or direct oxidation by ozone.

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